

5 PROCESS FOR THE PREPARATION OF A THERMOPLASTIC ELASTOMER
 COMPRISING A PARTIALLY VULCANIZED RUBBER CONCENTRATE

The invention relates to a process for the preparation of a thermoplastic elastomer.

10 A process for the preparation of thermoplastic elastomers is for example known from "Compounding of rubber Concentrate Thermoplastic Vulcanizates" by Terry M. Finerman, Ph.D., Luc Vandendriessche, Joseph E. Pfeiffer, presented at the Society of Plastics Engineers Topical Conference TPEs 2000, September 28-29, 1999. Described is the preparation of fully vulcanized rubber concentrates and of thermoplastic elastomers by melt mixing the fully vulcanized
15 rubber concentrates with ingredients such as oil, filler, stabilizers, processing aids and thermoplastic polymers for example polypropylene or polyethylene. The thus obtained thermoplastic elastomers have the disadvantage that their mechanical properties are not sufficient for some applications for example in automotive, building and construction, mechanical rubber goods or consumer products. For example the tensile
20 strength value of those thermoplastic elastomers is relatively low and therefore not meeting the required automotive material specifications. Another disadvantage of the above process is that the preparation of fully cured rubber concentrates with consistent properties and good morphology is difficult because of the high concentration of elastomeric phase and the minor concentration of thermoplastic phase.

25 The object of the present invention is to completely or largely eliminate the stated drawbacks.

This object is achieved in that the thermoplastic elastomer is prepared by melt mixing:

- 30 a. a partially vulcanized rubber concentrate
 b. a thermoplastic polymer and/or additives
 c. optionally oil and
 d. a curing agent.

35 Surprisingly the process of the present invention provides the preparation of thermoplastic elastomers with improved mechanical properties which meet the stringent material specifications needed for some applications in automotive, building and construction, mechanical rubber goods or consumer products. A further advantage is that the elastic properties of the thermoplastic elastomer are improved.

Moreover the thermoplastic elastomers show an improved fluid resistance. Yet another advantage is that thermoplastic elastomers may be prepared with a better compression set.

5 The partially vulcanized rubber concentrate (a) is prepared by melt mixing:

- e. at least one elastomer and optionally oil
- f. at least one thermoplastic polymer
- g. a curing agent.

10 The elastomer(s) and optionally oil and the thermoplastic polymer(s) are melt mixed and kneaded above the melting point of the thermoplastic polymer whereby the elastomer is vulcanized during mixing and kneading. This process is also known as a dynamic vulcanization process.

15 The elastomer (e) may be any elastomer capable of being vulcanized by the curing agent. Examples of elastomer(s) are ethylene-propylene copolymers, hereinafter called EPM, ethylene-propylene-diene terpolymers, hereinafter called EPDM, acrylonitrile-butadiene rubber, styrene-butadiene rubber, isobutene-isoprene rubber, styrene-ethylene/styrene-butadiene block copolymers, butyl rubber, isobutylene-p-methylstyrene copolymers or brominated isobutylene-p-methylstyrene copolymers or natural rubber. Preferably, the elastomer in the partially vulcanized
20 rubber concentrate according to the invention is an olefinic elastomer. It is especially preferred to use EPM or EPDM as elastomer. More preferably, EPDM is used as elastomer. The EPDM preferably contains 50-70 parts by weight ethylene monomer units, 48-30 parts by weight alpha-olefin monomer units and 1-12 parts by weight monomer units originating from a non-conjugated diene or combinations of more than
25 one non-conjugated diene. Preferably the alpha-olefin is propylene. As non-conjugated diene use is preferably made of dicyclopentadiene (DCPD), 5-ethylidene-2-norbornene (ENB) or vinylnorbornene (VNB). The elastomer(s) may be prepared for example with a Ziegler-Natta catalyst, a metallocene catalyst or a single site catalyst.

30 The elastomer for example comprises between 0-250 parts of oil per 100 parts of elastomer. Preferably comprises between 20-200 parts per 100 parts of elastomer. It is especially preferred to comprise between 30-160 parts of oil per 100 parts of elastomer. Any known oil may be used, examples of oils are processing oils for example paraffinic, naphtalenic or aromatic oil or isoparaffinic oil which is also known as polyalphaolefinic oil. Preferably a highly hydrogenated oil obtained by a hydrocracking
35 and isodewaxing process is used, for example PennzUltra, 1199, supplied by Pennzoil

in the United States of America. The point in time at which the oil is metered is not critical. In the process, the oil is for example added before, during or after the dynamic vulcanisation of the elastomer. It is also possible that the oil is added partly before and partly during and/or after the dynamic vulcanisation of the elastomer. It is also possible
5 that the elastomer has been pre-mixed with the desired quantity of oil or a proportion thereof. In fact a person skilled in the art can adjust the ratio of elastomer(s) /thermoplastic polymer(s)/oil to achieve partially vulcanized rubber concentrates with a low hardness. The partially vulcanized rubber concentrate for example has a hardness of 70 shore A or lower measured according to ASTM D-2240. Preferably the hardness
10 is 60 shore A or lower. Most preferably the hardness is 50 shore A or lower.

Examples of suitable thermoplastic polymers (f) which may be used in the preparation of the partially vulcanized rubber concentrates are thermoplastic polyolefin homo- and copolymers or blends thereof. For example homopolymers of ethylene or propylene, copolymers of ethylene and propylene, copolymers of ethylene
15 and an alpha-olefin comonomer with 4-20 carbon atoms or copolymers of propylene and an alpha-olefin comonomer with 4-20 carbon atoms. In case of a copolymer, the content of propylene in said copolymer is preferably at least 75 % by weight. The thermoplastic polyolefin homo- and copolymers may be prepared with a Ziegler-Natta catalyst, a metallocene catalyst or with another single site catalyst. Also suitable
20 thermoplastic polymers are for example reactor thermoplastic polyolefine elastomers (TPO's), polyamides, polycarbonate, polyesters, polysulfones, polylactones, polyacetals, acrylonitrile-butadiene-styrene (ABS) resins, polyphenylene oxide (PPO), polyphenylene sulfide (PPS), styrene-acrylonitrile (SAN) resins, polyimides, styrene maleic anhydride (SMA) and aromatic polyketones. It is possible to use more than one
25 thermoplastic polymer in the preparation of the partially vulcanized rubber concentrates.

Preferably, a polypropylene homopolymer is used as thermoplastic polymer. The polypropylene may be atactic, isotactic, syndiotactic or a physical and chemical mixture thereof. The term chemical mixture means that the polypropylene
30 may have atactic, isotactic or syndiotactic structures randomly or in blocks along the molecular chains. The polypropylene homopolymer may be linear or branched. The Melt flow index (MFI) of the polypropylene preferably is between 0.3 and 50; more preferably below 20 (according to ISO norm 1133 (230°C; 2.16 kg load)).

Examples of suitable curing agents (g) include sulfur, sulfurous
35 compounds, metal oxides, maleimides, phenol resins and peroxides. The curing agents

may be used with or without accelerators. Said curing agents are for example described in US-A-5100947. It is also possible to use siloxane compounds as curing agent, for example hydrosilane or vinylalkoxysilane. The elastomer is preferably vulcanized with a phenol resin, a siloxane or a peroxide. .. Examples suitable

5 accelerators are sulphur, ethylene dimethylacrylate, polyethylene glycol dimethylacrylate, trimethylol propane trimethacrylate, divinyl benzene, diallyl itaconate, triallyl cyanurate, diallylphtalate, allyl methacrylate, cyclohexyl methacrylate and m-phenylene bismaleimide.

The amount of curing agent, the accelerator, the temperature and the
10 time of vulcanisation are selected in order to obtain the desired degree of vulcanization. Preferably the amount of curing agent is between 0,1-10 parts by weight per 100 parts by weight of elastomer. More preferably the amount of curing agent is between 0,1-5 parts by weight per 100 parts by weight of elastomer.

The degree of vulcanization of the elastomer can be expressed in
15 terms of gel content or conversely, extractable components. The gel content is the ratio of the amount of non-soluble elastomer and the total amount of elastomer (in weight) of a specimen soaked in an organic solvent for the elastomer. The method is described in US-A-4311628 and US-A-5100947. In general terms a specimen is soaked for 48 hours in an organic solvent at temperatures suitable for the thermoplastic polymer and
20 the elastomer. The solvent should be capable of dissolving the thermoplastic polymers completely at the temperature of gel test. After weighing of both the specimen and the residue the amount of non-soluble elastomer and total elastomer are calculated, based on knowledge of the relative amounts of all components in the composition.

The elastomer in the rubber concentrate is partially vulcanized. Partially vulcanized
25 means that the elastomer may be vulcanized to a relatively low degree as long as there is no problem with pellet stickiness. Preferably the elastomer in the partially vulcanized rubber concentrate has a gel content higher than 50 %. More preferably a gel content higher than 70 %.

The partially vulcanized rubber concentrate is preferably prepared by
30 melt mixing between 30-95 parts by weight of the elastomer(s), between 0-70 parts by weight of oil, between 5-50 parts by weight of the thermoplastic polymer(s), between 0,1-10 parts by weight of the curing agent per 100 parts by weight of elastomer, whereby the sum of the parts by weight of the elastomer(s), thermoplastic polymer(s), curing agent and oil is 100. More preferably the amount of elastomer(s) varies between
35 35-90 parts by weight, the amount of oil varies between 5-60 parts by weight , the

amount of curing agent varies between 0,1-5 parts by weight per 100 parts by weight of elastomer and the amount of thermoplastic polymer(s) varies between 5-40 parts by weight, whereby the sum of the parts by weight of the elastomer(s), thermoplastic polymer(s), curing agent and oil is 100. Most preferably the amount of elastomer(s) varies between 40-85 parts by weight, the amount of oil varies between 10-50 parts by weight, the amount of curing agent is between 0,1-5 parts by weight per 100 parts by weight of elastomer and the amount of thermoplastic polymer(s) varies between 5-30 parts by weight, whereby the sum of the parts by weight of the elastomer(s), thermoplastic polymer(s), curing agent and oil is 100.

The process for the preparation of the thermoplastic elastomer according to present invention comprises melt mixing

- a. the partially vulcanized rubber concentrate
- b. a thermoplastic polymer and/ or additives
- c. optionally oil and
- d. a curing agent.

The melt mixing may be carried out in conventional mixing equipment for example roll mills, Banbury mixers, Brabender mixers, continuous mixers for example a single screw extruder, a Buss kneader, Ferro continuous mixer (FCM) and a twin screw extruder. Preferably melt mixing is carried out in a twin screw extruder with sufficient mixing efficiency, good temperature control and residence time control. By the use of a twin-screw extruder good tensile properties are achieved. More preferably the melt mixing is carried out in a single screw extruder. By the use of a single screw extruder better compression set values may be achieved. The use of a single or twin screw extruder depends on the desired properties the thermoplastic elastomer should have.

The partially vulcanized rubber concentrate, the thermoplastic polymer and/or the additives, the oil and the curing agent may be dry blended prior to the melt mixing. Alternatively the partially vulcanized rubber concentrate, the thermoplastic polymer and/or the additives, the oil and the curing agent may be directly fed by feeders to the continuous mixer.

Examples of the thermoplastic polymers (b) which may be melt mixed with the partially vulcanized rubber concentrate (a) are chosen from the above described thermoplastic polymers (f). The choice of the thermoplastic polymer in terms of melt flow index or viscosity depends on the end applications. A person skilled in the art may select the thermoplastic polymer with proper molecular weight, molecular

weight distribution or molecular structure to achieve the thermoplastic elastomer with balanced properties.

Examples of oils (c) which may be used in the process of the present invention are processing oils for example paraffinic, naphtalenic or aromatic oil or isoparaffinic oil which is also known as polyalphaolefinic oil. Preferably a highly hydrogenated oil obtained by a hydrocracking and isodewaxing process is used, for example PennzUltra, 1199, supplied by Pennzoil in the United States of America. The point in time at which the oil is metered is not critical. In the process, the oil is for example added before, during or after the dynamic vulcanisation of the thermoplastic elastomer. It is also possible that the oil is added partly before and partly during and/or after the dynamic vulcanisation of the thermoplastic elastomer.

Examples of the suitable curing agents (d) are described above as the curing agents (g). The curing agent may be in powder form, in liquid form or may be soluble in a liquid. If the curing agent is in powder form the partially vulcanized rubber concentrate pellets may first be coated with a processing oil and then blended with the curing agent powder prior to melt mixing with the thermoplastic polymers. If the curing agent is in liquid form, it may be dry mixed with the partially vulcanized rubber concentrate prior to melt mixing with the thermoplastic polymer and /or the additives. If the curing agent is soluble in a liquid for example in processing oil or a solvent it may first be dissolved in the liquid and then coated onto the rubber concentrate pellets prior to melt mixing with the thermoplastic polymers. Alternatively, liquid curing agent, curing agent solution in oil or solvent, or curing agent melt can be dosed or injected directly to the mixer in the form of a liquid or liquid solution.

Examples of additives which may be melt mixed are reinforcing and non-reinforcing fillers, plasticizers, antioxidants, stabilizers, processing oil, antistatic agents, waxes, foaming agents, pigments, flame retardants and other known agents described in for example the Rubber World Magazine Blue Book. Examples of fillers that may be used are calcium carbonate, clay, silica, talc, titanium dioxide, and carbon. Another additive that may optionally be used in the thermoplastic elastomer is a Lewis base for example a metal oxide, a metal hydroxide, a metal carbonate or hydrotalcite. The quantity of additive to be added is known to one skilled in the art.

In the process of the present invention it is also possible to prepare the thermoplastic elastomer by melt mixing the partially vulcanized rubber concentrate, additives and curing agent without the thermoplastic polymer. In this case suitable additives are viscosity modifiers, low friction coefficient additives such as silicon oil and

fatty amide lubricants, tackifiers or the additives as described above. The amount of additives is for example between 0,5-15 parts by weight relative to the total quantity of the thermoplastic elastomer. Preferably the amount of additives is between 1-10 parts by weight relative to the total quantity of thermoplastic elastomer. More preferably the amount of additives is between 2-8 parts by weight relative to the total quantity of the thermoplastic elastomer.

The gel content of the thermoplastic elastomer according to the present invention may vary between 60 and 100%. Preferably, the gel content is in excess of 80%. More preferably, the gel content is in excess of 90%. Most preferable the gel content is in excess of 97%.

The process of the present invention comprises the preparation of the thermoplastic elastomer by melt mixing for example:

- a. 10-90 parts by weight of the partially vulcanized rubber concentrate
- b. 90-10 parts by weight of a the thermoplastic polymer and/or additives
- c. 0-30 parts by weight of oil
- d. 0,1-10 parts by weight of the curing agent

whereby the sum of the parts by weight of the partially vulcanized rubber concentrate, the thermoplastic polymer and/or additives, the oil and the curing agent is 100.

- Preferably the thermoplastic elastomer is prepared by melt mixing
- a. 15-70 parts by weight of the partially vulcanized rubber concentrate
 - b. 30-85 parts by weight of a the thermoplastic polymer and/or additives
 - c. 0-30 parts by weight of oil
 - d. 0,1-5 parts by weight of the curing agent

whereby the sum of the parts by weight of the partially vulcanized rubber concentrate, the thermoplastic polymer and/or additives, the oil and the curing agent is 100.

The process of the present invention may be carried out in two stages. In a first stage, the partially vulcanized rubber concentrate may be prepared whereby at least one elastomer is partially vulcanized in the presence of at least one thermoplastic polymer using appropriate curing agents. In a second stage the partially vulcanized rubber concentrate, the appropriate thermoplastic polymer and/ or additives are melt-mixed in the presence of the curing agent to initiate a further dynamic vulcanization. The curing agents used in the first and in the second stage may be the same or different curing agents. Preferably the same curing agent is used in the two stages.

The two stages can be carried out independently in separate steps or

sequentially in the same processing equipment. After dynamic vulcanization the thermoplastic elastomer may be pelletized. The thermoplastic elastomer may however also be directly fed in molten stage to next processing equipment for example through a die. In such case the continuous mixer is attached with the die or other necessary downstream equipment and acts not only as mixer but at the same time as a melting and a conveying equipment for processes as foaming, film and sheet extrusion, profile extrusion, film and sheet calendering or co-extrusion.

The additives may be added during the preparation of the partially vulcanized rubber concentrate or during the preparation of the thermoplastic elastomer or both.

The thermoplastic elastomer prepared by the process according to the present invention may be used in automotive, building and construction, mechanical rubber goods or consumer products.

The present invention will be further explained by the following examples without being limited thereto. The measurements in the examples were carried out using the following tests:

Hardness ASTM D-2240, 5 sec delay

Tensile strength, ASTM D-412, Die C

Ultimate Elongation, ASTM D-412, Die C

100% modulus, ASTM D-412, Die C

Tear strength, ASTM D-624, Die C

Compression set, 22hrs@ 70C % ASTM D-395, method B

Compression set, 70hrs@125C % ASTM D-395, Method B

Oil swell, 70 hrs@125C, ASTM D-471

Example 1

A partially vulcanized rubber concentrate (compound 1) was prepared in a 92 mm Werner&Pfleiderer intermeshing co-rotating twin-screw extruder by melt mixing and kneading 67,1 parts by weight Keltan P597™ (50 wt% oil-extended EPDM) with 7,7 parts by weight polypropylene homopolymer PP 1012™ (MFI=1.2) as thermoplastic polymer, 25,2 parts by weight of Sunpar 150C™ processing oil, 0,3 wt% phenolic resin SP1045™ and 0,3 wt% stannous chloride dihydrate activator. The properties of compound 1 are shown in table 1.

Table 1

<u>Properties</u>	<u>Test value</u>
Hardness, Shore A	41
Tensile strength, Mpa	3,1
Elongation %	424
100% Modulus, Mpa	1
Tear Strength, kN/m	11,6
Compression set, 22 hrs@70 C, %	25
Compression set, 70 hrs@125 C, %	35,5
Oil swell in IRM 903, 70 hrs@125 C, %	125

Example 2

5 A thermoplastic elastomer (compound 2) was prepared of compound 1 pellets and a polypropylene homopolymer 31S07A (MFI=0,7) without the addition of phenolic resin SP1045™ as curing agent. Compound 2 was prepared on a 25mm Berstorff intermeshing co-rotating twin screw extruder.

10 Example 3

 A thermoplastic elastomer (compound 3) was prepared of compound 1 pellets and a polypropylene homopolymer 31S07A (MFI=0,7) with the addition of phenolic resin SP1045™ as curing agent..

15 To prepare compound 3, the compound 1 pellets were first coated with a small amount of processing oil Sunpar 150C™ and then blended with SP1045 powder in a cement mixer before the polypropylene homopolymer 31S07a was introduced. All ingredients were further dry blended using a cement mixer prior to the melt mixing.

20 Compound 3 was prepared on a on a 25mm Berstorff intermeshing co-rotating twin screw extruder.

Example 4

 A thermoplastic elastomer (compound 4) was prepared according to example 3 except that a 1.5 inch Killion single screw extruder with l/d ratio of 24/1 was

used.

After melt mixing, melt strands were cooled in a cold water bath before being pelletized. All compounds were dried for at least three hours to remove any residual moisture prior to injection molding.

- 5 4x4 cm plaques with a thickness of 3 mm were used for testing the mechanical properties. The results are shown in table 2

Table 2

	Compound 2	Compound 3	Compound 4
	Parts by weight	Parts by weight	Parts by weight
compound 1	58,6	58	58
PP homopolymer 31S07A	41,4	41,2	41,2
Sunpar 150C™		0,2	0,2
phenolic resin SP1045™		0,6	0,6
Hardness Shore D	39,4	41	39,1
Tensile strength, MPa	14,8	18,2	13,3
Ultimate Elongation, %	728	580	493
100% modulus, MPa	8,8	9,8	8,6
Tear strength, kN/m	73,3	73,6	67
Compression set, 22hrs@ 70C, %	57,5	52,3	45,3
Compression set, 22hrs@ 125C, %	76,7	69,1	68
Oil swell in IRM 903, 70 hrs@125C, %	44,4	32	36,7

- Table 2 shows that the thermoplastic elastomers prepared by the process of the present invention have good mechanical properties. Moreover it is clear that the use of a twin-screw extruder leads to better mechanical properties whereas the use of a single screw extruder leads to better compression set values. In addition, the use of the curing agent in the preparation of compounds 3 and 4 shows improved fluid resistance as indicated by the lower oil swell values in comparison to the control compound 2.
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